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(54) Title: **STRENGTHENED CERAMIC RESTORATION**

(57) Abstract: The present invention relates to a process for the preparation of a full-ceramic dental restoration, comprising heat pressing of a tooth coloured pressing glass on a fully or partially supporting structure of yttria doped tetragonal zirconia (YTZP), comprised of yttria doped tetragonal zirconia ceramic having a grain size, as measured by the linear intercept method, of less than 0.6 µm, wherein the pressing glass has a thermal expansion coefficient (TEC) of between 9.0 and 11.0 µm/m.K (measured in the range of from 25 to 500°C) and wherein the pressing glass has a pressing temperature of between 750 and 1000°C. In a further aspect, the invention relates to a full-ceramic dental restoration, comprising a fully or partially supporting structure of yttria doped tetragonal zirconia (YTZP) and a heat pressed tooth coloured pressing glass, which restoration is modelled to be in occlusal contact with opposing teeth and in mesio-distal contact with neighbouring teeth.

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Title: Strengthened ceramic restoration

The present invention relates to an aesthetic ceramic dental restoration, and particularly to a crown, part-crown or a bridge. In addition, the invention relates to a process for manufacturing such a product. More specifically, the present invention concerns a process for the production of an  
5 aesthetic heat-pressed restoration in occlusion, which is strengthened by a zirconia suprastructure, as well as the product obtainable in this way.

Dental restorations are mostly metal-ceramic composite structures, comprising a metallic framework used for load bearing, and ceramic or porcelain coatings for aesthetic appearance. More in detail, nowadays, about  
10 80% of all fixed restorations are metal-ceramic restorations; these metal ceramic restorations show a clinical survival rate of at least 95% after 7.5 years.

In the vast majority of manufacturing processes, the ceramic material is applied by using repeated layer formation. Particularly, a layer of  
15 ceramic or porcelain is applied, followed by firing or sintering, which steps are repeated until the suitable dental restoration is obtained. During this conventional process, each consecutive layer of porcelain shrinks during sintering. This shrinkage makes it very hard to obtain proper occlusal contacts with the antagonist teeth.

20 It would be very desirable to find a cost and time saving process compared to the traditional porcelain layering process.

Another disadvantage of the conventional layering technique is that often defects such as bubbles or clefts are formed, having an adverse effect on the adhesion between porcelain and either translucent layer or core or support  
25 material.

In the prior art, attempts have been made to solve or reduce these problems. In this light, reference can be made to an article titled "Gießen,

pressen, modellieren" published in DZW (Woche) 23/02. In this reference, a process is described for preparing a dental restoration in occlusion, wherein a cast metal structure is first covered with two opaque liner layers, followed by waxing-up up till the occlusal contacts with the opposing teeth and mesio-  
5 distal contacts with the neighbouring teeth are obtained. Sprues are attached to the wax part, the restoration is embedded in a refractory material and a tooth coloured glass ceramic is pressed onto the metal prestructure. Because of the non-translucent nature of the metal, the metal shimmers through the translucent outer glass ceramic which results in an less attractive looking  
10 restoration.

Beside the fact that these known metal-ceramic combinations show limitations concerning aesthetic appearance, the last years, the use of metals in the oral cavity has been disputed due to their biological incompatibility risk. This led to the need for bio-inert, metal free dental restorations.

15 In the art, it was proposed to meet this need by making all-ceramic dental restorations or prostheses. Such all-ceramic dental restorations have been made of feldspathic porcelain, leucite re-inforced porcelain, alumina, glass-infiltrated porous alumina and glass ceramics. These ceramic materials show, however, low bend strengths and toughness, which properties imply  
20 design restrictions, non-reliability and complicated multistep manufacturing procedures for, e.g., dental bridges.

Based on these findings, the person skilled in the art has focussed its attention to zirconia base materials to replace the metal base, because zirconia has promising properties in respect of durability and longevity.

25 Reference can be made to the article of Filser *et al.* titled "All-Ceramic Dental Bridges by Direct Ceramic Machining (DCM)" as published in: Materials in Medicine, Materials Day, Department of Materials, Eds. M.O. Speldel; P.J. Uggowitzer; vdf Hochschulverlag AG, ETH Zürich; Zürich (1998) 165-189  
Zirconia structures can be produced by slib casting or by milling. Because of

the opaqueness of zirconia, a tooth-coloured dental glass is used to bring the proper natural aesthetics to the zirconia base.

The zirconia used is mostly partially stabilized zirconia, and more in detail tetragonal zirconia stabilized with yttria, which has high strength and  
5 toughness.

The starting powder for these ceramic restorations has special demands for particle size and morphology as described in detail in the article of Filser *et al.*. These demands are necessary for an homogeneous result on the consolidation by isostatic pressing at a pressure higher than 2000 bar. Blocks  
10 are subsequently partially sintered at 900°C until the powder particles are bonded by neck growth to give the ceramic body strength high enough to be able to mill it. Milling is done taking account of an enlargement factor that corresponds to the expected sintering shrinkage in the final sintering step. The zirconia structure is then coated with a veneer porcelain to meet the patient's  
15 requirements concerning colour and translucency.

In EP-A-0 631 995, all-ceramic restorations are prepared by pressing and heating a combination of 50-99 wt.% ceramic and 1.50 wt.% glass in a mold. Although it is preferred in the invention of EP-A-0 631 995 to use alumina powder and/or zirconia powder as ceramic, also yttrium stabilized  
20 zirconia is mentioned. Further, it is indicated that the aesthetic character of the prosthesis can be improved by veneering the ceramic/glass composite. The veneering composition is not applied by pressing, nor described in detail.

Although the traditional layering technique could be used, thermal pressing of dental glass into a lost wax form is a more effective and economic  
25 way.

Cornelissen gives in TTM: Magazine voor Tandartsen en Tandtechnici 10 (2001) and in Quintessenz Zahntech. 28(2) (2002), 150-158, a description of the Cordent crown. This crown is prepared by directly modelling the entire dentine form inclusive crown shoulder to an AGC Galvano yellow  
30 cap, embedding in refractory, pressing ceramic, and debedding, followed by

divesting and glazing firings. The yellow metal cap is said to provide a nice deep orange glow at the occlusal and near the edges. Cornelissen notes that in the Cordent crown the advantages of all-ceramic systems are combined with the advantages of metal-ceramic systems.

5               Processes are described whereby a wax model is embedded in a refractory material and after hardening of the mould the wax is burnt-out. A glass material in the form of a dense pellet is brought in over the pressing connector channels and with a refractory cylinder under thermal plastification the pellet is pressed in the mould.

10              These materials lack sufficient strength to be used for more stressed applications such as bridges.

                In accordance with the present invention full-ceramic dental restorations are prepared which meet all needs sketched combined with the advantages of the described prior art systems. Other advantages and benefits  
15 of the present invention will become clear after reading the following description.

                More in detail, the present invention relates to a process for the preparation of a full-ceramic dental restoration, which should be in occlusal contact with opposing teeth and in mesio-distal contact with neighbouring  
20 teeth, comprising heat pressing of a tooth coloured pressing glass on a fully or partially supporting structure of yttria doped tetragonal zirconia (YTZP), comprised of yttria doped tetragonal zirconia ceramic having a grain size, as measured by the linear intercept method, of less than  $0.6\text{ }\mu\text{m}$ , wherein the thermal expansion coefficient (TEC) of the pressing glass lies between 9.0 and  
25  $11.0\text{ }\mu\text{m/m.K}$  (measured in the range of from 25 to  $500^{\circ}\text{C}$ ) and the pressing temperature of the pressing glass lies between  $750$  and  $1000^{\circ}\text{C}$ .

                In a further aspect, the present invention relates to a full-ceramic dental restoration, comprising a fully or partially supporting structure of yttria doped tetragonal zirconia (YTZP) and a heat pressed tooth coloured pressing  
30 glass, which restoration is modelled to be in occlusal contact with opposing

teeth and in mesio-distal contact with neighbouring teeth. Preferably, this full-ceramic dental restoration is obtainable by the process of the present invention.

Surprisingly, it was found according to the present invention that a  
5 tooth coloured glass ceramic when pressed on a strong zirconia structure,  
which has a certain degree of translucency, a very naturally looking  
restoration can be obtained, even when no liner was used. The zirconia used is  
referred to in the above-mentioned article of Filser *et al.*, and described in  
more detail by Lüthy in W.H. Mörmann (ed.), CAD/CIM in Aesthetic Dentistry,  
10 Quintessenz, Chicago, (1996), 229 ff., and has a high strength and can be used  
for support structures in single element restorations as well as in larger  
constructions such as 3 to 4-unit bridges.

The ability to heat-press a tooth coloured glass ceramic onto such a  
structure means an enormous time saving when compared to the layering of  
15 porcelain powder and subsequently sintering the powder as is usual in the  
traditional way. This cost and time saving is in comparison to the tradition  
porcelain layering process. During this latter process each consecutive layer of  
porcelain shrinks during sintering making it very hard to obtain proper  
occlusal contacts with the antagonist teeth.

20 Because the press-pellet is already in a tooth colour, the colour of the  
restoration will not vary from the given colour as can be the case when  
layering with a variety of colours. The colouring of the porcelain used in the  
present invention is known to the person skilled in the art. A suitable method  
is described in detail in DE-OS-199 04 522, which document is incorporated by  
25 reference in the present description for describing the method of colouring.

It is for instance possible to apply pure oxidic pigments on the  
zirconia, followed by the sintering together of the zirconia and oxidic pigments.  
In a particular embodiment, the pigments are pressed with a binder into a  
block or cylinder to be used as a pensil to bring the pigments on the zirconia  
30 surface.

In another embodiment, the partially sintered zirconia structure is impregnated with a solution of metal chlorides, nitrates, acetates or alcoholates and, subsequently dried and sintered to obtain a tooth coloured zirconia structure after sintering. Very suitable results are obtained, while using  
5 metals of the group of iron, praesodimium, nickel, cerium, erbium, cobalt, and copper.

In a preferred embodiment, the supporting structure is densely sintered; preferentially, the ceramic is produced by CAD/CAM technology. More specifically, in a preferred embodiment of the process of the invention the  
10 ceramic is milled by a CAD/CAM-system in the green state or in a partially sintered state, followed by sintering to full density.

In the process of the invention very good results are obtained with a supporting structure formed from electrophoretic deposition of zirconia from a slurry, followed by sintering to full density.

15 In another embodiment, the structure is milled out of an hot isostatically hopped zirconia.

Apart from the above, the German "Patentschrift" 196 30 412 and the corresponding US-A-5,833,464 teach a process for the fabrication of a full-ceramic dental build-up on a zirconia root pin, wherein a zirconia-glass is heat-  
20 pressed against the root pin that has a TEC that is the same or up to 3.0  $\mu\text{m}/\text{m.K}$  higher than the TEC of the zirconia glass. These prior art documents also describe the build-up with zirconia glass of a tooth replacement without mentioning how the zirconia is used. No reference is made to occlusal restorations, as is the subject of the present invention. Moreover, the zirconia  
25 glass described in the German and U.S. patent has low transparency and cannot be used for aesthetic tooth-like restorations, as is the case with the present invention.

The process of the invention directly presses the occlusal contacts in an aesthetically working material after the occlusal contact with the

antagonistic teeth and the mesio-distal contacts with the neighbouring elements having been precisely modelled in wax in the traditional way.

Another advantage over the traditional layering is the high density, low defect structure that can be obtained by pressing a densely sintered glass instead of applying a porcelain as a powdery substance with subsequent  
5 sintering. The latter shows very seldom a bubble-free structure.

Another advantage over the traditional layering is the adhesion obtained between the translucent material and the zirconia core. During layering the boundary layer often shows defects such as bubbles and clefts,  
10 while the pressed on glass shows an excellent defect free boundary, resulting in a better adhesion and a higher structural strength.

For particular embodiments, advantages can be obtained when a conventional liner is applied to the supporting zirconia structure which liner has a melting point less than 50°C lower than the pressing temperature of the  
15 pressing glass.

The process offers another advantage in the possibility of directly pressing a shoulder with a perfect fitting margin, without showing the substructure at the edge of the supporting material. For this the edge of the supporting core is kept short by 0.5 to 2 mm from the edge.

20 The process of the invention has the advantage of the possibility to create a chameleon effect, when using the heat press ceramic as shoulder material (Figure 3; Right). Because the wax has been applied after the zirconia structure is fitted on the gypsum die, the wax-up for the shoulder can follow the die exactly around the margin, and the subsequently pressed shoulder  
25 reproduced in glass ceramic will have the same good fit. In the traditional way involving several steps of layering porcelain, several corrections with porcelain additions have to be made to produce a fitting margin, because of the shrinkage of the porcelain powder during sintering.

In a particular aspect of the process of the invention, the structure  
30 is, hence, kept short by 0.5 to 2.0 mm from the edge of the final restoration to



be made, after which the pressing glass is pressed in such a way that it forms an aesthetically pleasing shoulder without showing the core at the margin.

Preferably, the stresses are transferred on the core only, while leaving the shoulder free from the prepared tooth.

5           The present inventors have found that the stability of the adhesive bond strength between the glass and the zirconia is critically dependent upon the susceptibility of the zirconia material to low temperature degradation (LTD). Although YTZP zirconia ceramics are known to have a high strength and toughness, they are also known to be susceptible to strength degradation  
10 upon exposure to steam in the temperature range of about 100-500°C. The origin of this LTD phenomenon is attributed to a reaction involving water and the Zr-O-Zr bonds of the ceramic. This reaction causes transformation of zirconia grains from their desired tetragonal state to the monoclinic state. This transformation is accompanied by a volume expansion in the transformed  
15 grain of about 4 vol.%, which causes microcracking in the component and, accompanied, strength degradation.

Without wishing to be bound by any theory, it is believed that the environmental conditions present in the mouth are such that LTD may occur in the zirconia dental components and that this phenomenon may have a  
20 negative impact on the strength of the YTZP-dental glass bond. In particular, the temperatures in the mouth are typically simulated by thermal cycling between about 5 and 55°C. Although these temperatures are somewhat below those typically associated with the LTD phenomenon, Chevalier *et al.* (see: Bioceramics 10 Ed. L. Sedel and C. Rey (Proc. of the 10<sup>th</sup> Int. Symp. on  
25 Ceramics in Medicine, Paris, France, October 1997) Elsevier Science Ltd.) have suggested that LTD may also occur in some YTZP zirconias at temperatures as low as about 37°C. Thus, it is believed that LTD may act upon YTZP in dental systems. With regard to YTZP-glass bonds, it is believed that LTD of the YTZP may cause general microcracking in the vicinity of the transformed grain and  
30 in particular at the uncracked surface of YTZP material, and that this

microcracking degrades the adhesive bond strength of the glass-zirconia system and allows for further ingress of water into the zirconia material, thereby accelerating the spread of LTD.

The selections made in the process of the present invention prevent  
5 or at least inhibit or reduce LTD.

In said article of Chevalier *et al.* suitable yttria-stabilised zirconias for use in the present invention are identified.

Very good results are obtained in a process, wherein the connector to the press pellet reservoir and the specimen is formed by a continuous flow  
10 plate of 1.5 to 2.5 mm thick. This embodiment will be described in more detail in Figure 8 and the accompanying text.

The present invention will now be described in more detail, wherein reference is made to the drawings, wherein:

Figure 1 shows a schematic overview of a zirconia structure with  
15 wax-up;

Figure 2 shows the zirconia structure of Fig 1 after pressing;

Figure 3 shows final restorations with a liner and with a zirconia shoulder (prior art) and with a shoulder of heat-pressed ceramics in accordance with the present invention;

20 Figure 4 shows a flow scheme for the production of zirconia structures to be used in the present invention;

Figure 5 shows a flow scheme for the production of the pressing step wherein pressing glass is brought on the zirconia structures according to the present invention;

25 Figure 6 shows a microphotograph of a dental glass pressed to YTZP zirconia in the absence of a liner;

Figure 7 shows a microphotograph of a dental glass pressed to YTZP zirconia covered with a liner; and

Figure 8 shows a special flow plate for a pressed glass structure.

All of the above mentioned advantages are provided by the present invention which comprises the process of producing an esthetic heat-pressed restoration in occlusal and mesio-distal contact with neighbouring and opposing teeth, strengthened by a fine grained yttria doped tetragonal zirconia (YTZP) support structure.

The new glass composition that was produced has a pressing temperature from about 750 to 1000°C, and preferably from 900 to 950°C and has a coefficient of thermal expansion of from about 9.0 to 11.0, and preferably from about 9.0 to 10.0  $\times 10^{-6}/^{\circ}\text{C}$  (25°C to 500°C).

More specifically, the present inventors have found a low expansion glass or preferably a glass-ceramic material suitable for over-pressing a zirconia suprastructure such as a crown, part-crown or bridge has been developed.

Taking into account the guidances given herein above, the glass used in the process of the invention preferably has the following chemical composition: 7-15 wt.%  $\text{Al}_2\text{O}_3$ , 13-23 wt.% of ( $\text{K}_2\text{O} + \text{Na}_2\text{O}$ ), 1-3 wt.% of ( $\text{BaO} + \text{CaO}$ ), 1-3 wt.% ( $\text{Sb}_2\text{O}_3 + \text{Li}_2\text{O}$ ), and 0.2-1.2 wt.% fluor, the balance being  $\text{SiO}_2$ , and colouring compositions. In a more preferred embodiment, the glass has the following chemical composition: 7-15 wt.%  $\text{Al}_2\text{O}_3$ , 6-14 wt.%  $\text{K}_2\text{O}$ , 5-11 wt.%  $\text{Na}_2\text{O}$ , 0.2-2.5 wt.%  $\text{BaO}$ , 0.1-1.5 wt.%  $\text{CaO}$ , 1.2-2.5 wt.%  $\text{Sb}_2\text{O}_3$ , 0.05-0.5 wt.%  $\text{Li}_2\text{O}$ , and 0.5-1.0 wt.% fluor, the balance being  $\text{SiO}_2$ , and colouring compositions.

Low expansion glasses for use in the present invention can be produced by blending powdered metal oxides or carbonates or nitrates in the appropriate proportions. The blended powders are fused to form a glass melt followed by quenching, drying, ballmilling and sieving by means known in the art.

The powder formed from these glasses have a particle size of preferably less than 106  $\mu\text{m}$ ; they are pigmented to obtain a toothlike appearance. Then the powder is granulated with a binder and uniaxially dry-

pressed at room temperature and then sintered at a temperature of 800° to 1000°C., preferably 900° to 960°C, for 1 minute to 1 hour, preferably 1 minute to 30 minutes.

The glass-ceramic pellet obtained in this way can then be over-pressed on a zirconia suprastructure embedded in the mould to obtain a restoration in occlusal contact with the opposing teeth and mesio-distal contacts with neighbouring teeth. A suitable embedding material is silica-based refractory such as Carrara® Press Speed (ex Elephant Dental B.V., Netherlands).

The zirconia supporting structure is prepared from yttria doped tetragonal zirconia. This stabilized zirconia should have a grain size, as measured by the intercept method, of less than 0.6  $\mu\text{m}$ . Very good results are obtained when using a partially stabilized zirconia with a density of more than 99.0 wt.%, and preferably more than 99.5%, such as 99.8% of the theoretical density with an open porosity of less than 0.4% and preferably less than 0.2%. The elasticity modulus was not higher than 220 GPa and the fracture toughness was at least 5 MPa.m<sup>1/2</sup>.

Not suitable were partially stabilized zirconias (PSZs) such as magnesia stabilized zirconias (Mg-PSZ) or calcia-stabilized zirconias (Ca-PSZ). These zirconias are characterized by a coarsely grained structure (of the order of about 50  $\mu\text{m}$ ) containing significant residual intragranular porosity. In addition, due to the high sintering temperature needed to sinter PSZs, impurity diffusion at the grain boundaries often produces a significant glassy phase, thereby affecting mechanical properties. The weak intergranular bonds of the coarse PSZ grains are more easily broken during adhesion testing, thereby lowering overall bond strength. In contrast, the very fine microstructure of biomedical grade YTZP materials results in very strong intragranular bonding. For this reason YTZP appeared a material providing a surface suitable for bonding to heat-pressed glass. Preferably, the YTZP ceramic has a grain size of less than 0.5  $\mu\text{m}$ .

If desired, the zirconia structure can be coloured by ionic or complex containing solutions which contain rare earth elements or elements of the adjacent group. The partially sintered zirconia structure can for instance be dipped in such a solution, dried and sintered to its final density.

5           Figure 4 shows a production flow scheme for the zirconia structures for use in the present invention. Particularly, the zirconia powder is subjected to isostatic pressing, preferably using CAD/CAM technology. The pressed form is subjected to partial sintering and subsequently milled, although it can also be milled in green state, preferably using a CAD/CAM system. After milling  
10 the oversize, the formed structure is sintered to full density giving the zirconia substructure.

This substructure is further treated following the scheme shown in figure 5. The substructure and a wax-up occlusion (see Figure 1) are invested in refractory. The wax is burnt out, and the mould is preheated. Glass pellets  
15 are pressed in the mould, after which the investment is removed (see Figure 2). The product formed can be subjected to a treatment to glaze its surface.

In Figure 3, two final restorations of the present invention are described. The left-hand image shows a zirconia shoulder structure coated with a liner on which a low expansion glass of the invention is pressed.  
20 Thereto a suitable liner, for instance one consisting of 54.8 wt.% SiO<sub>2</sub>, 12.9 wt.% Al<sub>2</sub>O<sub>3</sub>, 11.5 wt.% K<sub>2</sub>O, 8.7 wt.% Na<sub>2</sub>O, 10.4 wt.% CeO<sub>2</sub>, 1.0 wt.% Li<sub>2</sub>O and 0.4 wt.% B<sub>2</sub>O<sub>3</sub>; or one consisting of 58.5 wt.% SiO<sub>2</sub>, 12.6 wt.% Al<sub>2</sub>O<sub>3</sub>, 11.0 wt.% K<sub>2</sub>O, 7.1 wt.% Na<sub>2</sub>O, 10.4 wt.% CeO<sub>2</sub>, 0.4 wt.% Li<sub>2</sub>O, was applied in a single coat of 20 to 40 µm onto a densely sintered zirconia support-structure and fired  
25 at 800°C and 915°C for both liners illustrated respectively.

The liner-coated zirconia coping was waxed up and sprued as described before. The substructure comprising the liner was subsequently overpressed with the glass material.

The right-hand image of Figure 3 shows a zirconia substructure with  
30 a shoulder in heat-pressed glass ceramics.

It was additionally found that when a special flow plate (fig 8) was used to guide the flowing heat-pressed glass a better filling was obtained with less material, that with separate sprues as is usual in the traditional technique. The plate is 1.5 to 2.5 mm thick and starts from one side with the  
5 press pellet reservoir and is over its full length in contact with the pressed specimen. The flow plate is easier to separate with the appropriate cutting wheels than the much thicker separate sprues in the traditional technique. The plate makes contact with the pressed specimen in a place where it does not interfere with the contact surfaces to the antagonistic teeth and the mesio-  
10 distal contact areas.

The present invention will be illustrated in more detail in the following, non-limiting examples. Where reference is made to percentages, weight percentages drawn to the weight of the final composition are meant, unless otherwise indicated.

15

#### Examples 1-4

Low expansion glasses or glass-ceramic materials suitable for over-pressing a zirconia suprastructure such as a crown, part-crown or bridge were  
20 prepared. Thereto, four mixtures were produced by blending powdered metal oxides or carbonates or nitrates in the appropriate proportions. The blended powders were fused to form a glass melt followed by quenching, drying, ballmilling and sieving by means known in the art (see Table 1 for the final compositions).

25

The powder formed from either one of the four undermentioned glasses having a particle size of less than 106  $\mu\text{m}$  are pigmented to obtain a toothlike appearance. Then the powder was granulated with a binder and uniaxially dry-pressed at 900°C for 20 minutes.

A partially stabilized zirconia with a density of 99.8% of theoretical  
30 density with an open porosity of less than 0.2% was obtained by following the

method depicted in figure 4. The elasticity modulus was about 200 GPa and the fracture toughness was about 5 MPa.m<sup>½</sup>.

The glass-ceramic pellets obtained as described were over-pressed on the zirconia suprastructure embedded in a mould to obtain a restoration in  
5 occlusal contact with the opposing teeth and mesio-distal contacts with neighbouring teeth.

Table 1. Composition of heat-press glass ceramic

Component	Ex. 1	Ex. 2	Ex. 3	Ex. 4
SiO <sub>2</sub>	66.2	65.0	67.4	66.0
Al <sub>2</sub> O <sub>3</sub>	10.7	7.5	13.9	14.4
K <sub>2</sub> O	9.5	12.2	6.8	9.1
Na <sub>2</sub> O	8.5	9.6	7.4	6.8
BaO	1.2	2.0	0.4	0.4
CaO	0.7	0.2	1.3	1.1
Sb <sub>2</sub> O <sub>3</sub>	2	2.3	1.8	1.5
Li <sub>2</sub> O	0.2	0.4	0.1	0.2
F	0.8	0.9	0.7	0.6
Pressing temperature, °C	900	800	940	930
Thermal Coefficient of Expansion (TCE), x10 <sup>-6</sup> /°C (25°C to 500°C)	9.5	11.0*	8.7	10.1
Break strength of incisor tooth, N (without liner)	5200	5800	6300	6200
Break strength of incisor tooth, N (with liner B)	N.D.	N.D.	N.D.	6000
Thermal Shock Tests, nr. of cycles up to 20 until cracks appear	20	Cracks	Cracks	20

\* TCE was measured from 25°C to 400°C

N.D. = not determined

5

A liner material A, consisting of 54.8 % SiO<sub>2</sub>, 12.9 % Al<sub>2</sub>O<sub>3</sub>, 11.5 % K<sub>2</sub>O, 8.7 % Na<sub>2</sub>O, 10.4 % CeO<sub>2</sub>, 1.0 % Li<sub>2</sub>O and 0.4 % B<sub>2</sub>O, was applied in a single coat of 20 to 40 µm onto a densely sintered zirconia support-structure and fired at 800°C.

10

The liner-coated zirconia coping was waxed up and sprued as described before.

15

Upon overpressing a zirconia-structure embedded in a silica-based refractory form (Carrara® Press Speed, Elephant Dental B.V., Netherlands) with densely sintered pellets having the oxidic composition of Ex. 4, the liner layer melted and dripped to the margin area.

Another liner material B, consisting of 58.5 % SiO<sub>2</sub>, 12.6 % Al<sub>2</sub>O<sub>3</sub>, 11.0 % K<sub>2</sub>O, 7.1 % Na<sub>2</sub>O, 10.4 % CeO<sub>2</sub>, 0.4% LiO<sub>2</sub> was applied in a single coat of 20 to 40 µm and fired at 915°C. After the liner was overpressed using the



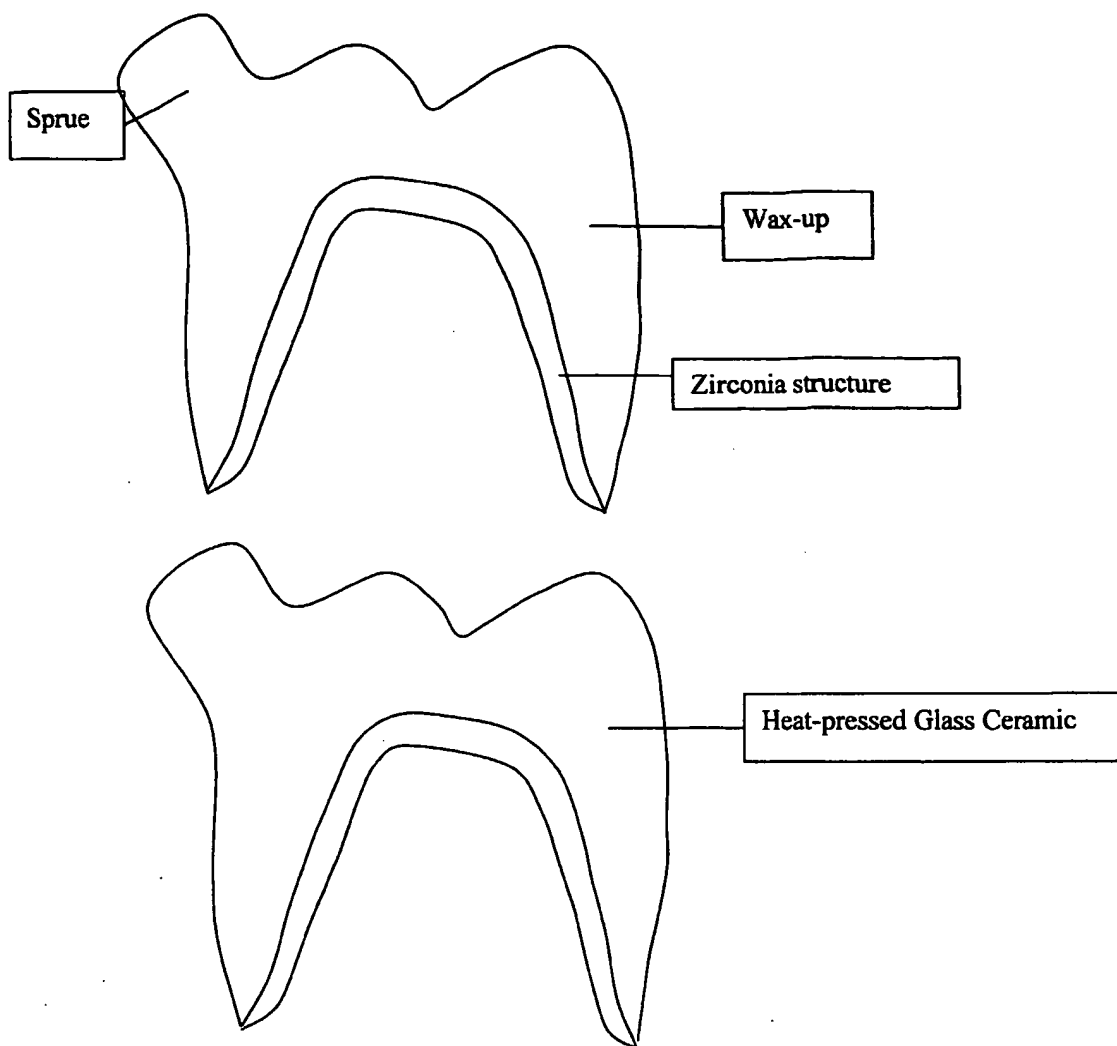
same pellets as described above testing the liner material A, the layer remained in place and good results were obtained regarding both the thickness of the liner over the whole surface of the zirconia coping as for a good esthetic appearance.

- 5           The interfaces formed were studied in cross section. The results are shown by the microphotographs in Figures 6 and 7.

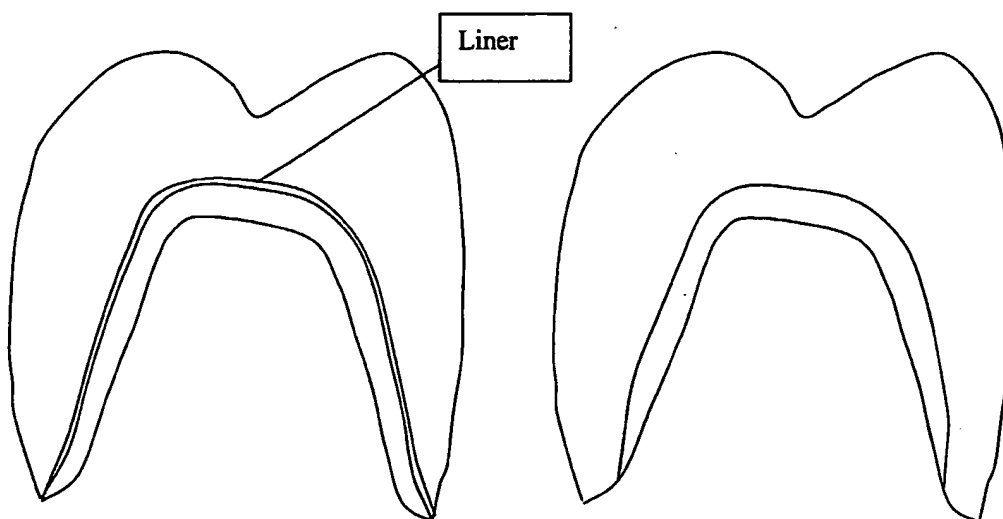
Claims

1. Process for the preparation of a full-ceramic dental restoration, comprising heat pressing of a tooth coloured pressing glass on a fully or partially supporting structure of yttria doped tetragonal zirconia (YTZP), comprised of yttria doped tetragonal zirconia ceramic having a grain size, as  
5 measured by the linear intercept method, of less than  $0.6\text{ }\mu\text{m}$ , wherein the pressing glass has a thermal expansion coefficient (TEC) of between  $9.0$  and  $11.0\text{ }\mu\text{m/m.K}$  (measured in the range of from  $25$  to  $500^{\circ}\text{C}$ ) and wherein the pressing glass has a pressing temperature of between  $750$  and  $1000^{\circ}\text{C}$ .
2. The process according to claim 1, wherein the supporting structure  
10 is comprised of densely sintered ceramic produced by CAD/CAM technology.
3. The process according to claim 2, wherein the ceramic is milled by a CAD/CAM-system in the green state or in a partially sintered state, and subsequent sintering to full density.
4. The process according to claim 1 or claim 2, wherein the supporting  
15 structure is milled out of a hot isostatically pressed zirconia.
5. The process according to claim 1, wherein the supporting structure is formed by electrophoretic deposition of zirconia from a slurry, followed by sintering to full density.
6. The process according to claim 1, wherein the structure is kept short  
20 by  $0.5$  to  $2.0\text{ mm}$  and the pressing glass is forming an aesthetically pleasing shoulder without showing the core at the margin.
7. The process according to any one of the claims 1-6, wherein a liner is applied to the supporting zirconia structure with a melting point less than  $50^{\circ}\text{C}$  lower than the pressing temperature of the pressing glass.
- 25 8. The process according to any one of claims 1-7, wherein the connector to the press pellet reservoir and the specimen is a continuous flow plate having a thickness of  $1.5$ - $2.5\text{ mm}$ .

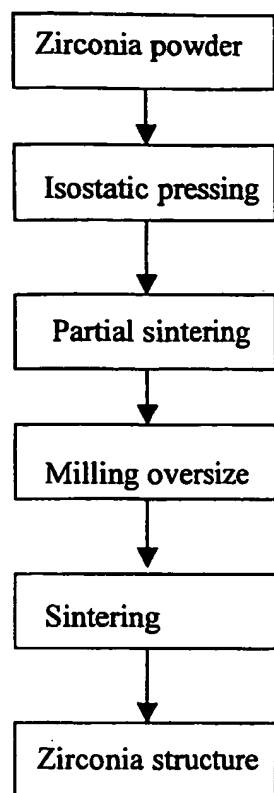
9. Full-ceramic dental restoration, comprising a fully or partially supporting structure of yttria doped tetragonal zirconia (YTZP) and a heat pressed tooth coloured pressing glass, which restoration is modelled to be in occlusal contact with opposing teeth and in mesio-distal contact with
- 5 neighbouring teeth.
10. The full-ceramic dental restoration of claim 9, obtainable by the process of any one of the claims 1-8.



**Figure 1 and 2: Zirconia structure with wax-up (1) and after pressing (2)**



**Figure 3. Left: Final restoration with a zirconia shoulder and a liner. Right: with a shoulder in heat-pressed glass ceramics.**

**Figure 4. Production flow for zirconia structures**

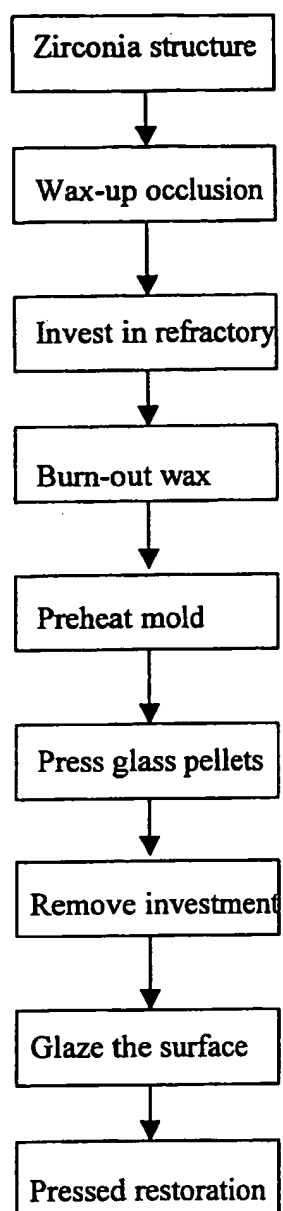
**Figure 5. Production flow Press-To-Zirconia**



Figure 6. Dental Glass pressed to YTZP zirconia without the use of a liner



Figure 7. Dental Glass pressed to YTZP zirconia covered with liner B

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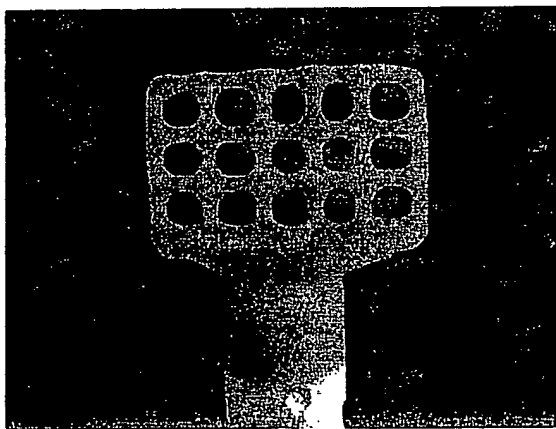


Figure 8. Special flow plate to a pressed glass structure

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/AL 03/00616

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 A61C13/00 A61C13/08 A61K6/06 C04B41/50

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61C A61K C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	EP 0 218 853 A (TORAY INDUSTRIES) 22 April 1987 (1987-04-22) column 3, line 14 - line 21 column 13, line 9 - line 21 examples claims	1-10
A	US 2002/006532 A1 (ROBIN ARNAUD) 17 January 2002 (2002-01-17) paragraphs '0023!', '0024! claims	1-10
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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